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GB 1502979 A	GB 1387454 A	EP 0346059 A2
EP 0342781 A2	JP 550123618 A	US 4944823 A
US 4521544 A	US 4505778 A	US 4490517 A
US 4317752 A	US 4197372 A	US 3919017 A

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(54) Biodegradable composite material and process of producing same

(57) A biodegradable composite material includes a solid body of a natural polyhydroxy polymer, and a polyurethane or a polymer of a vinyl monomer bonded to the solid body by reaction with part of the hydroxyl groups of the polyhydroxy polymer. The polyurethane or the polymer of a vinyl monomer is present in an amount of at least 10 % based on the weight of the solid body. The polyurethane-containing composite material is produced by reacting the solid body with a reaction solution of a polyisocyanate and a polyol compound. The natural polymer may be selected from cellulose, hemicellulose, lignocellulose, lignin and starch. The solid body may be in the form of a fibre, powder, film, sheet plate, block, pellet or rod. The composite material may be a foamed body wherein the solid body is in powder or fibre form. The vinyl monomer is graft polymerised onto the solid body.

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Background of the Invention

This invention relates to a biodegradable composite material and a process for the production thereof.

There is an increasing demand for biodegradable polymeric materials which may be usable as a substitute for plastics such as polyolefins which are not decomposed by microorganisms. While natural polyhydroxy substances such as cellulose and starch are biodegradable, the mechanical properties thereof are so poor that it is impossible to utilize them in place of plastics.

Summary of the Invention

It is an object of the present invention to provide a biodegradable material having satisfactory mechanical properties.

Another object of the present invention is to provide a simple process which can impart excellent mechanical properties to a solid, natural polyhydroxy polymer while retaining the inherent biodegradability thereof.

In accordance with one aspect of the present invention, there is provided a biodegradable composite material comprising a solid body of a first, natural polymer having a multiplicity of hydroxyl groups, and a second, synthetic polymer selected from the group consisting of polyurethanes and those of a vinyl monomer and bonded to said solid body by reaction with part of the hydroxyl groups of said first polymer, the amount of said second polymer being at least 10 % based on the weight of said solid body.

In another aspect, the present invention provides a process for the preparation of a biodegradable composite material, comprising the steps of:

providing a solution containing a polyol compound and a polyisocyanate compound;

reacting a solid body of a natural polymer having a multiplicity of hydroxyl groups with said solution to form polyurethane chains chemically bonded to said solid body by reaction with part of the hydroxyl groups.

Other objects, features and advantages of the present

invention will become apparent from the detailed description of the preferred embodiment of the present invention to follow.

Detailed Description of the Preferred Embodiment of the Invention

The biodegradable composite material according to the present invention includes a solid body of a natural polymer containing hydroxyl groups. Examples of the natural polymers include cellulose, hemicellulose, lignocellulose, lignin and starch. The solid body may be in the form of a fiber, powder, a film, a sheet, a plate, a block, a pellet, a rod or any other desired shape.

To the solid body are chemically bonded molecules of a polyurethane or a polymer of a vinyl monomer by reaction with part of the hydroxyl groups of the natural polymer. It is important that the amount of the polyurethane or the polymer of a vinyl monomer should be at least 10 % by weight, preferably 15-300 % by weight based on the solid body, since otherwise the mechanical properties of the solid body are not satisfactory.

The polyurethane-containing, biodegradable composite material may be produced by reacting the above-mentioned solid body of a natural polymer having a multiplicity of hydroxyl groups with a solution containing a polyol compound and a polyisocyanate compound to form polyurethane chains chemically bonded to the solid body by reaction with part of the hydroxyl groups of the solid body.

Any polyisocyate compound conventionally used for the formation of polyurethanes may be used for the purpose of the present invention. Aliphatic polyisocyanates, alicyclic polyisocyanates, aromatic polyisocyanates and modified products of these polyisocyanates may be generally used. One preferred example of the aliphatic polyisocyanate is hexamethylene diisocyanate. One preferred example of alicyclic polyisocyanates is isophorone diisocyanate. Examples of the aromatic polyisocyanates include tolylene diisocyanate, xylylene diisocyanate, diphenylmethane diisocyanate, polymeric diphenylmethane diisocyanate, triphenylmethane triisocyanate and

tris(isocyanatophenyl)thiophosphate. Illustrative of suitable modified polyisocyanates are urethane prepolymers, hexamethylene diisocyanate Biuret, hexamethylene diisocyanate trimer and isophorone diisocyanate trimer.

Any polyol compound conventionally used for the production of polyurethanes may be used for the purpose of the present invention. Examples of such polyol compounds include low molecular weight polyols such as ethylene glycol, diethylene glycol, 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, trimethylolpropane, glycerin, triethanolamine and sorbitol; polyether polyols such as polyethylene glycol, polypropylene glycol, polytetramethylene glycol and ethylene oxide/propylene oxide copolymers; polyesters such as polycaprolactone, polyβ-methyl-γ-butylolactone and those obtained from diols and dibasic acids. Liquid polybutadiene containing hydroxyl groups, polycarbonate diols and acryl polyols may also be used as the polyol compounds.

Solvent soluble, natural polyhydroxy polymers such as lignocellulose, organosolv lignin, explosion lignin, cellulose and hemi-cellulose may also be used as a part of the polyol to be reacted with the polyisocyanate. Such natural polyhydroxy polymers can form a hard segment of the polyurethane as described in United States patent No. 4,987,213 issued to Hirose et al, disclosure of which is hereby incorporated by reference.

In performing the above reaction of the solid body, the polyisocyanate is used in such an amount that the equivalent of the isocyanate groups of the polyisocyanate is 0.8-2.0 times, preferably 1.0-1.5 times, that of the hydroxyl groups of the polyol compound and the solid body. If necessary, an inert solvent such as tetrahydrofuran, dioxane or dimethylsulfoxide may be used. Further, a conventional catalyst such as of Sn-series or amine-series may be used, if desired. The reaction of the solid body with the solution containing the polyol and polyisocyanate is generally performed at a temperature of 10-150 °C, preferably 20-120 °C.

When the solid body is in the form of powder, fiber chips or the like small size solid, the composite material can

be suitably formed into a foamed article. The method for producing foamed articles is the same as that utilized for the formation of conventional polyurethane foams.

The biodegradable composite material containing a polymer of a vinyl monomer may be produced by reacting the above-mentioned solid body of a natural polymer having a multiplicity of hydroxyl groups with a vinyl monomer to form polymer chains of the vinyl monomer grafted on the solid body by reaction with part of the hydroxyl groups of the solid body.

The vinyl monomer to be used in the present invention may be, for example, an olefin such as ethylene, propylene, butene or butadiene, vinyl acetate, styrene, vinyl chloride, acrylonitrile, vinyl fluoride, an acrylic ester or an methacrylic ester. The vinyl monomer is dissolved in a suitable solvent such as water or methanol and the solution is reacted with the solid body of a natural polymer. If necessary, a catalyst such as Ce^{4+} or Fe^{2+}-H_2O_2 may be used. The graft polymerization is performed at 0-100 °C, preferably 10-80 °C.

Since the composite material according to the present invention uses a natural polymer, it shows good biodegradability. Further, since the composite material is not a mere mixture of a natural polymer with a synthetic resin but is an integrally chemically bonded substance, the mechanical properties thereof, such as tensile strength, are very high.

The following examples will further illustrate the present invention.

Example 1

Beech wood was digested at 180 °C for 5 hours in a cresol-water (8:2 vol/vol) mixed solvent, and the solvolysis lignin was separated from the cresol layer. After purification, 150 parts by weight of the solvolysis lignin were dissolved in 150 parts by weight of tetrahydrofuran. This solution (240 parts by weight) was mixed with 100 parts by weight of polymeric diphenylmethane diisocyanate to form a reaction mixture in the form of a solution. A filter paper was immersed in the reaction solution and impregnated therewith. The resulting filter paper

was then dried at room temperature and was disposed between a pair of stainless steel plates. The assembly was heated at 115 °C for 4 hours to obtain a composite sheet (Sample No. 2) having a polyurethane content of 15 % by weight. The above procedure was repeated in the same manner as described except that the concentrations of the solvolysis lignin and the diisocyanate were changed, thereby to obtain composite sheets (Sample Nos. 3-6) whose polyurethane contents are shown in Table 1. The thus obtained composite sheets and the raw material filter paper were tested for their stress-strain curves. The results were as summarized in Table 1.

Table 1

Sample No.	Polyurethane Content	Stress (MPa)		
		Strain (%)		
		2	2.5	3
1	0	4	4.25	4.5
2	15	10	10.5	11
3	28	12	14	15
4	54	17	18	19
5	79	20	21	22
6	86	22	24	26

Example 2

~~The solvolysis lignin (100 parts by weight) as shown in~~ Example 1, 100 parts by weight of polypropylene glycol (molecular weight: 400) and 100 parts by weight of tetrahydrofuran were mixed with each other to form a solution. This solution (200 parts by weight) was mixed with 100 parts by weight of polymeric diphenylmethane diisocyanate to form a reaction mixture in the form of a solution. In the same manner as described in Example 1, filter paper was reacted with th reaction mixture to form a composite sheet (Sample No. 8). The above procedure was repeated in the same manner while varying the concentrations of the reactants to obtain composite sheets (Sample Nos. 9 and 10). The thus obtained composite sheets and

the raw material filter paper were tested for their stress-strain curves. The results were as summarized in Table 2.

Table 2

Sample No.	Polyurethane Content	Stress (MPa)		
		Strain (%)		
		2	3	4
7	0	4	4.5	4.7
8	17	15	18	19
9	25	16	18.5	20
10	60	20	24	28

Example 3

Example 1 was repeated in the same manner as described except that wood tar distillation residues were used in lieu of the solvolysis lignin. The thus obtained composite sheets and the raw material filter paper were tested for their stress-strain curves. The results were as summarized in Table 3.

Table 3

Sample No.	Polyurethane Content	Stress (MPa)		
		Strain (%)		
		2	3	3.5
11	0	4	4.5	4.6
12	12	13	14	14.5
13	49	22	25	27
14	77	25	30	32

Example 4

Example 2 was repeated in the same manner as described except that wood tar distillation residues were used in lieu of the solvolysis lignin. The thus obtained composite sheets and the raw material filter paper were tested for their stress-strain curves. The results were as summarized in Table 4.

Table 4

Sample No.	Polyurethane Content	Stress (MPa)		
		Strain (%)		
		2	3	4
15	0	4	4.5	4.7
16	14	9	12	13
17	45	14	16	19
18	87	19	24	27
19	103	20	25	29

Example 5

Example 1 was repeated in the same manner as described except that polyethylene glycol (number average molecular weight: 400) was substituted for the solvolysis lignin solution, thereby obtaining an urethane-impregnated composite paper.

Example 6

100 Parts by weight of wood powder, 100 parts by weight of polyethylene glycol (number average molecular weight: 200), 1 part by weight of silicone oil, 0.5 part by weight of a Sn catalyst and 0.5 part by weight of water were mixed with each other, to which 200 parts by weight of polymeric diphenylmethane-diisocyanate were added, and the mixture was reacted to obtain a foamed body.

Example 7

Example 6 was repeated in the same manner as described except that cellulose powder was substituted for the wood powder, thereby to obtain a foamed body.

The invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof. The present embodiments are therefore to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims rather than by the foregoing description, and all the changes which come within the meaning and range of equivalency of the claims are therefore intend d to be embraced therein.

WHAT IS CLAIMED IS:

1. A biodegradable composite material comprising a solid body of a first, natural polymer having a multiplicity of hydroxyl groups, and a second, synthetic polymer selected from the group consisting of polyurethanes and those of a vinyl monomer and bonded to said solid body by reaction with part of the hydroxyl groups of said first polymer, the amount of said second polymer being at least 10 % based on the weight of said solid body.

2. A composite material as claimed in claim 1, wherein said first polymer is selected from the group consisting of cellulose, hemicellulose, lignocellulose, lignin and starch.

3. A composite material as claimed in claim 1, wherein said solid body is in the form of a fiber, powder, film, sheet, plate, block, pellet or rod.

4. A composite material as claimed in claim 1, wherein said second polymer includes a hard segment which is the reaction product of an admixture containing a polyisocyanate and a solvent solution of a natural polyhydroxy polymer.

5. A composite material as claimed in claim 1, and being in the form of a foamed body and wherein said solid body is in the form of powder or fibers.

6. A process for the preparation of a biodegradable composite material, comprising the steps of:

providing a solution containing a polyol compound and a polyisocyanate compound;

reacting a solid body of a natural polymer having a multiplicity of hydroxyl groups with said solution to form polyurethane chains bonded to said solid body by reaction with part of the hydroxyl groups.

7. A process as claimed in claim 6, wherein said polyol compound includes a natural polyhydroxy polymer and is dissolved in a solvent.

Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number 9205892.4

Relevant Technical fields

(i) UK Cl (Edition K) C3R; C3N; C3C; D1P (PFK,PDV, PDX,PFJ,PFX,PCBB)

(ii) Int CL (Edition 5) C08G, C08J, C08B, C08L, D06M

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii) ONLINE DATABASES: WPI

Date of Search

3 JULY 1992

Documents considered relevant following a search in respect of claims 1 (PART), 2 TO 7

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
X	GB 2220669 A (NATIONAL RESEARCH) - see Claims 1-5, Examples, page 1 lines 1-7, page 1 line 25 - page 3 line 13, page 6 lines 20-25	1,2,3
X	GB 2112791 A (EPSILON) - see whole specification	1,2,3
X	GB 1585074 (WADESON) - see whole specification	1,2,3
X	GB 1502979 (ELLINGSON TIMBER) - see claims, Examples, page 2 lines 29-39	1,2,3
X	GB 1387454 (BAYER)	1,2,3
X	EP 0346059 A2 (NATIONAL RESEARCH) - see whole specification, especially page 2 lines 33-49 Examples, Claims 1-5	1,2,3
X	EP 0342781 A2 (DIRECTOR-GENERAL) - see whole specification	1,2,3,5, 6,7
X	US 4944823 (CARBOCOL) - see column 3 lines 1-41, column 7 lines 44-50, Claims 1,2 Examples	1,2,3,6

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

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Examiner's report to the Comptroller under Section 17 (The Search Report)

Application number 9205892.4

Relevant Technical fields

(i) UK Cl (Edition) Contd. from page 3

(ii) Int CL (Edition)

Search Examiner

B J BALDOCK

Databases (see over)

(i) UK Patent Office

(ii)

Date of Search

3 JULY 1992

Documents considered relevant following a search in respect of claims

Category (see over)	Identity of document and relevant passages		Relevant to claim(s)
X	US 4521544	(CREHAN) - see column 5 lines 36-44	1 to 6
X	US 4505778	(ICI AMERICAS) - see column 1 line 52 to column 2 line 32, claims, Example 1	1,2,3
X	US 4490517	(OLIN) - see Examples, column 4 line 63 - column 5 line 2	1,2,3
X	US 4317752	(BLOUNT) - see column 1 line 44 - column 5 line 63, and Examples	1,2
X	US 4197372	(KRAUSE) - see claims and examples	1,2,5,6
X	US 3919017	(ELLINGSON) - see column 2 lines 24-47, claims and Examples	1,2,3
X	JP 550123618 A	(SANYO) - see WPI Accession No:- 80-79780C/45	1,2

Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

X: Document indicating lack of novelty or of inventive step.

Y: Document indicating lack of inventive step if combined with one or more other documents of the same category.

A: Document indicating technological background and/or state of the art.

P: Document published on or after the declared priority date but before the filing date of the present application.

E: Patent document published on or after, but with priority date earlier than, the filing date of the present application.

&: Member of the same patent family, corresponding document.

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